

NOTES ON SOLVENT EXTRACTION OF TORBANITE.

By J. A. DULHUNTY, B.Sc., Linnean Macleay Fellow of the Society in Geology.

(Plate vii; two Text-figures.)

[Read 19th August, 1942.]

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INTRODUCTION.

Considerable research work has been carried out on the extraction of coal with organic solvents at their boiling-points under atmospheric pressure, and also at higher temperatures under high pressure. The results of this work have been summarized by Bakes (1933). The best yields have been obtained by using solvents such as benzene, pyridine, tetraline and cyclohexanone. Extractions with benzene under pressure have yielded products amounting to 17% on a dry, ash-free basis, and with pyridine and tetraline yields as high as 35% have been obtained. The products of extraction appear to consist mainly of solid and oily bitumens, very little, if any, liquid hydrocarbons or true oils being present.

The action of solvents on coal which has been derived from vascular plant debris involves the extraction of sparingly soluble bitumens that form part of the coal substance, as well as the so-called "pyrobitumens" produced by heat. Solvent extraction of torbanite, derived from non-vascular organisms of a specialized nature, presents a somewhat different problem. The organic constituents, gelosite and retinosite, are extremely insoluble in all organic solvents at temperatures below 300°C. Extractions for long periods of time, using common solvents at their boiling-points, under atmospheric pressure, yield less than 1% of extract on an ash-free basis (Petrie, 1905). It has been found, however, that the organic matter of torbanite permanently changes to a soluble form as a result of heating at temperatures between 320° and 380°C., and particularly in the region of 360°C. This change in the vulnerability of the organic matter to solvent action accompanies the development of a pliable, or "rubbery", condition, which has been noted by many people and attributed to various causes. Early attempts to explain the pliable condition were based on the assumption that oily hydrocarbons were actually present in the torbanite, and it was suggested that these commenced to melt and become pliable before being distilled during retorting. It can now be shown by solvent extraction, that the products causing the pliable condition are quite different from the crude oil produced in retorting, and also from the organic matter originally present in the torbanite. The increase in solubility of certain oil shales, at temperatures above 300°C., was believed to be due to changes in the walls of the organic cells, allowing solvents to attack the substance of the cells as a whole. Microscopic examination of torbanite, preheated at 375°C., shows no evidence of physical change in the nature of

the cell walls. The results of research by recent workers indicate that a molecular rearrangement, or change, occurs in the organic matter of torbanite at a temperature of about 360°C., prior to the thermal decomposition into dry gas, oil vapour and carbon, which takes place during the later stages of retorting.

In 1932 the author, while carrying out retorting tests on Ulan and Baerami torbanites, first noted the development of the pliable condition due to this structural change, and the fact that the resulting rubbery mass could be partially dissolved in benzene, chloroform and kerosene, and consequently tests were made on the action of different solvents on preheated torbanite early in 1940. Later, Professor F. A. Eastaugh, of the University of Sydney, mentioned to the author that he had noted an increase in the susceptibility of torbanite to solvent action after heating above 300°C. Professor J. C. Earl, of the University of Sydney, also mentioned possible results from heating torbanite in the presence of a liquid at high temperatures. In 1941, Mr. L. J. Rogers, Department of Supply and Development, suggested the importance of investigating pressure-solvent extraction of torbanite, and Mr. R. F. Cane, National Oil Pty. Ltd., observed that the products responsible for the pliable condition in heated torbanite could be dissolved in common organic solvents. K. Luts (1934) noted an increase in the solubility of the "kerogen" in Esthonian algal limestone, at temperatures above 170°C., and described the formation of "bitumen" between 350° and 380°C. Experiments in the thermal solution of Volga and Gdov shales have been carried out by Russian workers (Diakova and Stepanzeva, 1940) who appear to have obtained successful results, although literature dealing with their investigations is not available at present in Australia. Early in 1942 the author, by special arrangement with the Linnean Society of New South Wales, commenced systematic quantitative research on solvent extraction of torbanite. This work was made possible by assistance from the Commonwealth Research Grant to the University of Sydney in obtaining special equipment, by generous co-operation of the Sydney Technical College in construction of high-pressure apparatus, and by valuable technical advice given by Mr. L. J. Rogers.

The preliminary results recorded in this paper deal with technique devised for quantitative solvent extraction of torbanite, pressure-benzole extraction, relations between temperature and the formation of soluble product, and the formation of soluble product at constant temperature.

APPARATUS.

The high-pressure vessel, illustrated in Fig. 1, was designed with the object of carrying out extraction under high pressure at temperatures above the normal boiling-points of solvents; heat treatment of torbanite at atmospheric pressure, or under high pressure generated by heating calculated quantities of liquids above their critical temperatures; and chemical treatment, including hydrogenation, of torbanite and products of extraction at high temperatures and pressures. The vessel is similar, in some respects, to the laboratory hydrogenation converter used in England by the Council for Scientific and Industrial Research at the East Greenwich Fuel Research Station. It was constructed from mild steel and designed to withstand a safe working pressure of 5,500 lb. sq. in. at ordinary temperatures, and 2,000 lb. sq. in. at an internal temperature of 500°C., using a safety factor of three. The lower flange and the body of the vessel were constructed from one piece of steel. The spigot head closing the cylinder is held in position and forced into the top of the cylinder by means of the top flange, which is bolted to the lower flange with eight 1½ in. bolts. The junction between the spigot and the cylinder is of the metal-to-metal, compression-line-seal type, consisting of upper and lower cones, turned on the spigot, at angles of about 8 and 20 degrees to the vertical, respectively, and one cone on the inside of the cylinder at an angle of about 12 degrees. The line-seal is obtained at the junction of the three cones, and it has proved very successful, requiring only a small pressure on the bolts between the two flanges.

A thermocouple sheath is provided by means of a blind tube screwed and welded to the inner surface of the spigot head, through which a ½ in. hole passes to the exterior. The pressure gauges and needle-valve are attached to the vessel by a tube

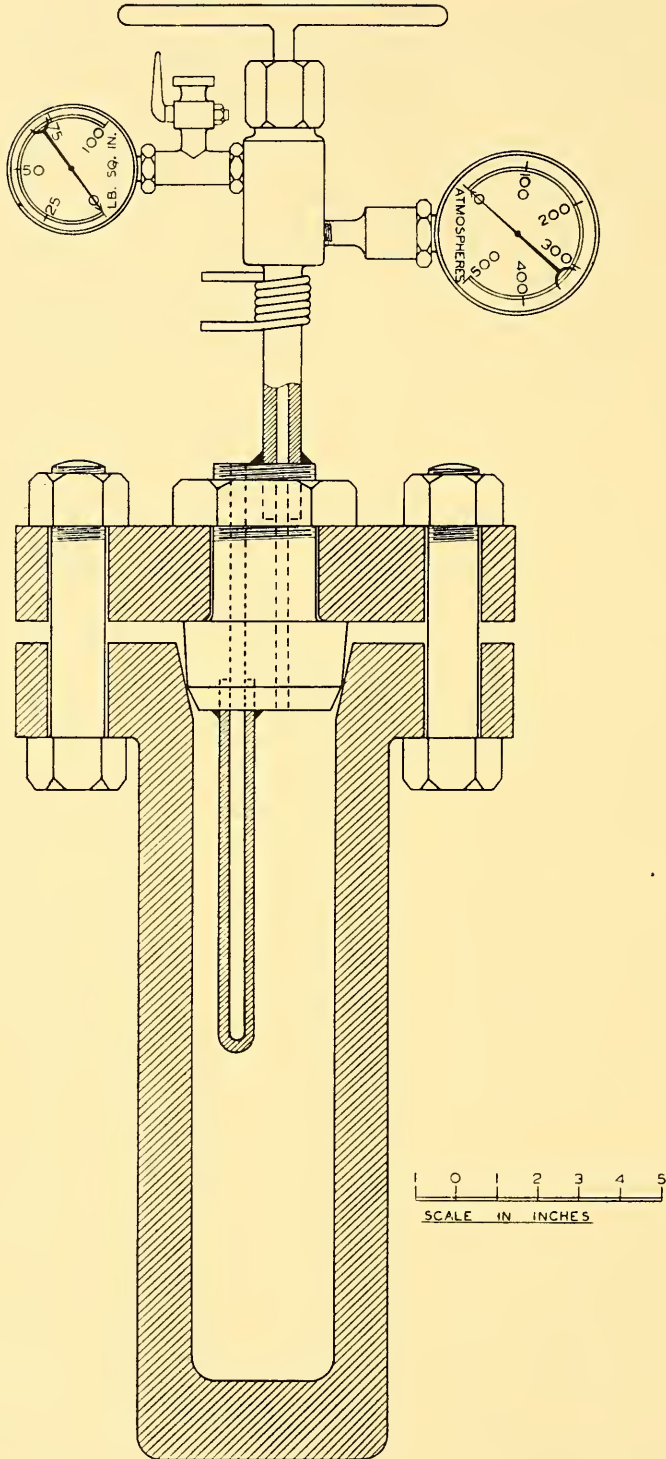


Fig. 1.—Section of high-pressure vessel used for solvent extraction of torbanite.

of $\frac{1}{4}$ in. bore, screwed and welded into the upper surface of the head, and connected with the cylinder by a $\frac{1}{4}$ in. hole through the spigot. The high-pressure gauge, situated below the needle-valve, is in direct communication with the cylinder. The low-pressure gauge, connected above the valve seat, is brought into operation only when the valve is opened. This gauge may be used for recording small residual pressures, at known temperature and constant volume, thus obtaining the volume of gas formed, or remaining unused, after an operation when it is too small to be recorded accurately on the high-pressure gauge.

The success of the cone-in-cone seal between the spigot and the cylinder depends on the formation of a narrow surface at the junction of the three cones. This surface tends to become wider each time the head is removed, and greater pressure is then required on the flange bolts to give an effective seal, making the head difficult to remove. To avoid this, provision was made for charging and discharging the vessel without removing the head. Gases can be charged through the cock on the connection to the low-pressure gauge. In the case of liquids, the needle-shaft is removed from the valve, and a fine metal tube inserted through the valve into the cylinder. The liquid is then introduced through the tube, allowing displaced air to pass out at the same time. Solid material in the form of powder can be injected by first mixing it to a paste with a suitable vehicle, and then pumping or washing it into the cylinder through a fine tube inserted at the valve. Liquids and powders can be discharged from the vessel by using a suction system attached to a tube, passing through the valve, to the base of the cylinder. The last of the powder can be washed from the cylinder by adding liquid at the valve, while the discharging system is still operating.

Liquid can be removed from the vessel by decantation, leaving a residue for further treatment. The solid material is allowed to settle, and then the liquid is pumped out by means of a fine tube, inserted through the valve, to a predetermined level near the base of the liquid layer. The remaining residue may be washed by lowering the tube to the base of the cylinder, and pumping in a measured quantity of liquid. The tube is then raised to the previous level, and the liquid again pumped out, after allowing the residue to settle. This may be repeated several times until sufficient of the original solution has been removed to meet the requirements of accuracy for the particular work being carried out.

If the vessel is to be used as an extractor, and continuous concentration and recirculation of solvent through the residue is necessary, as in the Soxhlet extraction system, the following procedure may be adopted:

An extraction thimble, containing the material to be extracted, is suspended immediately beneath the thermocouple sheath with a small funnel passing from the lower end of the sheath to the bottom of the thimble. The vessel is heated, and brought to constant temperature, which is maintained by means of an external thermocouple placed in the furnace. The internal thermocouple is then withdrawn, and a metal tube inserted in its place for the purpose of blowing a current of cool air into the sheath. This cools the sheath considerably, and condensation of the solvent occurs on its outer surface within the cylinder. The condensed solvent flows through the funnel to the extraction thimble, passes up through the material being extracted, and eventually overflows into the bottom of the cylinder, where the extract is concentrated as the solvent continues to vaporize.

During the extraction of very finely divided powders of low specific gravity, much solid material is carried over from the thimble to the base of the cylinder, as in the case of torbanite powder, which becomes finer as extraction proceeds. This difficulty has been overcome by dispensing with the extraction thimble, and using in its place a long funnel passing from the lower end of the thermocouple sheath to the bottom of the cylinder. The powder is then introduced into the cylinder and allowed to remain at its base, and the solvent, after condensing on the sheath, flows down through the funnel and passes up through the layer of powder.

PRINCIPLES OF HEAT TREATMENT AND EXTRACTION.

The physical and optical properties of gelosite and retinosite—the organically derived, oil-producing constituents of torbanite—have been described by the author (Dulhanty,

1939 and 1941*a*); and the physical effects of heat on these substances have been investigated (Dulhanty, 1941*b*). It is evident that the organic matter of torbanite has been derived from a specific type of original organic debris, which consisted essentially of microscopic unicellular algae. The transformation of the substance of the algae into the organic matter of torbanite took place over long periods of geological time, as a result of specialized conditions of burial and subsequent preservation. Extensive polymerization of organic molecules appears to have occurred during the change, giving rise to the hard, brittle and insoluble gelosite and retinosite of torbanite. The structural nature of these substances is, as yet, obscure; but it is certain that they may be looked upon as highly condensed masses of very large molecules, extremely resistant to solvent action and chemical attack, including atmospheric oxidation and natural weathering processes. It is difficult to dissolve more than 1% of the organic material by extraction with organic solvents at their boiling-points for long periods of time. Treatment with benzene, under pressure at a temperature of 270°C. for 24 hours, yields no more than 1.5% extraction of the organic constituents.

The whole success of solvent extraction of torbanite depends on the conversion of the insoluble organic matter to a soluble form by heat treatment. Heated at temperatures below 300°C., torbanite undergoes no apparent change, physically, microscopically or chemically. When heated between 300° and 400°C., particularly in the region of 345° to 360°C., a remarkable change occurs, rendering the organic material almost completely soluble in certain organic solvents, without the evolution of gases, or oil vapours, or the production of any microscopical changes of any consequence. A certain physical change, however, accompanies the formation of soluble products, and this is the development of the well-known pliable condition, or "rubberiness", which occurs prior to the evolution of oil vapours when torbanite is heated. At temperatures above 400°C., during the retorting process which is employed to obtain crude oil, thermal decomposition of the soluble material, or intermediate product, takes place, accompanied by the production of oil vapours, dry gas and carbon. It is evident that the soluble, intermediate products formed at about 360°C. are responsible for the development of the "rubbery" condition.

The nature of the change in the organic matter, from the insoluble to the soluble form, is not clearly understood; but the opinion of recent workers, including Mr. R. F. Cane, who has carried out excellent work on the thermochemical properties of the Glen Davis torbanite, favours the conception of a molecular rearrangement, or structural change. This change would appear to be only slight in relation to the molecular structure, but far reaching in its effects on the solubility of the material, and probably represents a partial depolymerization of the highly condensed mass.

It follows, from the foregoing discussion, that solvent extraction of torbanite may be carried out in two different ways. One method is to preheat the material at temperatures between 350° and 400°C., for a sufficient length of time to convert the organic matter to the soluble form, and subsequently extract at a lower temperature, using a solvent such as benzole with a low critical temperature, either at the normal boiling-point of the solvent under atmospheric pressure, or at higher temperatures under high pressure. The second method consists of extracting at the temperature necessary to produce the soluble material, which is 350°C. or higher, and removing the soluble products as they are formed. This could be accomplished at low pressure by using a solvent with a normal boiling-point higher than 350°C., or under high pressure, by using a solvent with a lower boiling-point, but possessing a critical temperature above 350°C.

The samples used for the extractions described later in this paper were prepared by powdering the torbanite until microscopic examination showed that the largest particles were smaller than the gelosite and retinosite bodies, which are about 0.01 in. in diameter, or fine enough to pass a 40 mesh I.M.M. sieve.

The physical changes which take place in the powder as a result of preheating and extraction, were examined on account of their importance in connection with the design of a suitable extractor. It was found that the powder showed no tendency to coke, or cohere, during preheating at temperatures up to 400°C., and extraction with benzole up to 270°C. The "rubbery" condition, caused by preheating, gives the powder a "springy" nature, and, although quite loose, it does not flow as readily as the unheated material. When heated above 400°C., the particles commence to cohere, and the powder

eventually fuses into a semi-liquid mass as thermal decomposition proceeds. This may be avoided, however, as temperatures above 400°C. are unnecessary in rendering the organic matter soluble.

The photomicrographs in Plate vii illustrate the effects of solvent extraction on preheated torbanite from Baerami and Glen Davis. In the original powders (Plate vii, A and B) the individual particles consist mainly of translucent gelosite and retinosite with small fragments of matrosite and humosite which formed the opaque groundmass in the torbanite. During extraction the gelosite and retinosite are removed, and the minute grains of the opaque insoluble constituents become separate particles. This causes the powder to become finer as extraction proceeds, until all the extractable material has been removed, and the residue consists of an extremely fine, black powder containing grains no larger than 0.005 in. (Plate vii, C and D). These grains, which possess an angular form caused by the grinding process, show no signs of coking, or rounding, due to solvent action. This indicates that the matrosite and humosite of torbanite are unaffected by preheating and solvent extraction.

THE SEPARATION OF SOLVENT FROM EXTRACTED PRODUCTS.

The suitability of a solvent for use in the extraction of torbanite depends on numerous factors, including its boiling-point, critical temperature, stability at high temperatures, solvent action, chemical reactivity towards the solute, properties determining its ease of separation from the extracted products and its economic possibilities. In obtaining the majority of the results recorded in this paper benzene was used as the solvent on account of its stability at high temperatures, good solvent properties, narrow boiling limits, relative chemical inertness and ease of separation from the extracted products. The solvent was prepared by fractionating commercial benzole and collecting the fraction boiling between 80° and 81°C.

Early attempts to separate the solvent from the soluble products, after extraction, consisted of concentrating the solution to small bulk by distilling off most of the benzene, and then drying the product under reduced pressure at temperatures between 60° and 100°C. All the solvent was removed in this way, but considerable quantities of the product were lost, due to the fact that small amounts of low-boiling hydrocarbons constitute part of the soluble product extracted from preheated torbanite. Attempts to remove the last of the solvent by chemical means were also unsatisfactory. It was found, however, that benzene could be separated from the extracted oils of low boiling-point by careful fractionation. Quantitative tests were carried out by adding measured quantities of benzene to crude oil produced by retorting torbanite, and to benzene-free extract obtained by chloroform and pyridine extraction. These mixtures were fractionated and in each case quantitative separations were effected. When solutions from benzene extraction were fractionated, it was found that the weights of extracted products agreed closely with the actual weight lost by the samples during extraction. They also agreed closely with the calculated loss based on proximate analyses of the fresh torbanite and residues after extraction.

It was concluded from the foregoing results that the quantitative separation of benzene and product could be satisfactorily carried out by fractionation, and the following simplified procedure was adopted as a routine method in determining the weight of product obtained by extraction:

The extract solution was placed in a flask fitted with a Golitedz still-head and immersed in an oil bath. The bulk of the benzene was distilled off between 79° and 85°C., and added to the solvent stock. The temperature of the residue was then gradually increased to 170°C., at which it was held until distillation ceased. On cooling, the residue was weighed as benzene-free product. The distillate boiling above 85°C. was refractionated with the object of separating the small quantity of product which distills over with the last of the benzene. It was found that this usually amounted to less than 3% of the total product. The product oxidizes readily, even at room temperature, with the formation of an insoluble product. This must be prevented as far as possible during the filtration and concentration of the extract solutions. If suction is used during the filtration, care should be taken to prevent air from passing through the residue before filtering and washing have been completed.

PRESSURE-BENZENE EXTRACTION OF PREHEATED TORBANITE.

Experiments in pressure-benzene extraction of preheated torbanite were carried out on a sample from the Glen Davis deposit. Tests were made to determine the advantage to be gained by using some means of circulating fresh solvent through the powder during extraction. It was found that the powder could not be retained in an extraction cup, as it became increasingly fine during extraction. It was also found that yields obtained by employing the method already described for returning condensed solvent to the base of the cylinder, and allowing it to flow up through the powder, were no greater than those obtained by merely placing the powder and solvent in the cylinder and exposing the flanges, at the head of the extractor, to the air outside the furnace. From this it was concluded that the slight cooling of the head caused condensation at the top of the cylinder and kept the solvent actually boiling, thus causing sufficient mixing of the powder and solvent to extract all the soluble products. Furthermore, the low specific gravity of torbanite, together with its expansion when heated (see Dulhunty, 1941*b*), facilitate the mixing of the powder and solvent.

In view of the foregoing results, no provision was made for circulation of fresh solvent during the extractions, which were carried out as follows:

The torbanite was crushed and ground to pass a 40 mesh I.M.M. sieve, and dried to constant weight at 120°C. After drying, 250 gm. of torbanite were mixed with benzene sufficient to wash the powder into the extractor, by the method already described, and additional benzene added to bring the total volume to 1,000 ml. Air was expelled from the extractor by boiling the solvent, with the valve open, until benzene commenced to condense at the outlet. The valve was then closed, and the temperature raised to 270°C., the pressure amounting to 560 lb. sq. in. This temperature was maintained for 16 hours, and then the extractor was cooled to 75°C., at which there was no residual pressure. After allowing the powder to settle, 700 ml. of solvent were drawn off from the liquid layer above the residue and filtered. The residue was then stirred and washed by adding 1,000 ml. of fresh solvent through a tube extending to the base of the cylinder. After allowing to settle for 2 hours, 1,000 ml. of liquid were again withdrawn, filtered and added to the original solution. It was calculated that two washings of 1,000 ml. each, under these conditions, would leave no more than 2% of the original solution in the extractor. Thus it was decided to wash twice with 1,000 ml. after each extraction.

The solution from the first extraction (described above), in which the torbanite had not been preheated, contained extracted product amounting to 0.75% of the total organic matter in the sample, i.e., on an ash-free basis.

The residue from the first extraction was then preheated at a temperature of 350°C. for 18 hours in the following manner:

The residue from the filtration of the first extract solution was returned to the extractor with 400 ml. of benzene, bringing the total volume to 700 ml. Air was expelled from the extractor, the valve closed and the temperature raised to 350°C., the pressure rising to 1,200 lb. sq. in. After maintaining this temperature for 18 hours, the extractor was cooled to 40°C., and the residual gas pressure, amounting to 13 lb. sq. in., was measured. This residual gas, occupying a volume of 4 litres at atmospheric pressure and room temperature, would represent, approximately, 2% by weight of the original sample on an ash-free basis.

A second extraction was then carried out, using 800 ml. of benzene at a temperature of 270°C. for a period of 8 hours. After cooling, the extract solution was withdrawn, and the residue washed twice with 1,000 ml. of benzene. The yield of product from this extraction was 74%, constituting a remarkable increase on the yield of 0.75% obtained in the first extraction before preheating.

The residue from the second extraction was then subjected to a second preheating at 400°C., under a pressure of 1,200 lb. sq. in. for a period of 5 hours, the total time above the temperature of the first preheating being 6½ hours. On cooling, there was no residual pressure at 75°C., which indicates that no low-boiling spirit, or dry gas, had been formed. A third extraction was then carried out, using 800 ml. of benzene at 270°C. for 8 hours. This extraction yielded 14% of product.

A proximate analysis of the residue at this stage gave 10.2% of volatiles, so it was preheated again at 400°C. for 2 hours, followed by extraction at 270°C. for 6 hours, which yielded an additional 2.1% of product.

The results of the foregoing extractions, together with Gray King Assay figures and proximate analyses (all of which were carried out on portions of the same sample) are summarized in Table I. The Gray King Assay was carried out at the laboratory of National Oil Pty. Ltd., Glen Davis, and represents the maximum oil yield under ideal retorting conditions.

TABLE I.
Comparison of Results of Solvent Extraction and Low Temperature Carbonization of Torbanite.

Treatment.	Yields in Per Cent. by Weight on Ash-free Basis.				Specific Gravity of Oil.	Oil Yield in Galls. per Ton.
	Oil.	Gas.	Organic Residue.	Total.		
Solvent extraction	90.1	1.0	11.7	102.8	0.92	172
Gray King retort	73.7	8.9	17.3	99.9	0.80	141

Sample.	Moisture.	Volatiles.	Fixed Carbon.	Ash.
Fresh torbanite. . . .	0.3	66.4	11.6	21.7
Extraction residue ..	—	6.5	19.5	74.0

It will be noted that the oil yield from solvent extraction is considerably higher than that obtained by retorting, and the amounts of dry gas and organic residue (mainly carbon) are correspondingly lower. This is due to thermal decomposition during retorting, in which process the soluble products (sp. gr. 0.92) are first formed between 350° and 400°C., and then cracked at temperatures above 400°C. into lighter oils (sp. gr. 0.85), gas and carbon, involving a loss of about 16% of the total organic matter. The yield by solvent extraction represents an increase of about 31 gallons per ton, or 22% by volume, on the yield from retorting. The extraction residue contained 6.5% of volatiles, which probably indicates the presence, in the original torbanite, of small quantities of organic matter derived from the vascular plant material which cannot be extracted by heat treatment and solvent action. The 19.5% of fixed carbon in the residue would represent coke formed by the decomposition of the insoluble vascular plant material, free carbon present in the torbanite in the form of mineral charcoal or fusain, and possibly small quantities of carbon formed during the conversion of the bulk of the organic matter to its soluble form.

RELATIONS BETWEEN TEMPERATURE AND FORMATION OF SOLUBLE PRODUCTS.

Experiments were carried out with the object of determining the relative amounts of soluble product formed by preheating the same sample at each of a series of increasing temperatures for a given length of time. In the procedure adopted 250 gm. of powdered torbanite were subjected to preheatings at temperature intervals of 20°C. from 300° to 420°C., and extracted with benzene under pressure after each heat treatment. Each preheating was carried out above the critical temperature of benzene, under pressure of its vapour, for a period of 2 hours at the preheating temperature, and a total period of 4 hours above the previous preheating temperature. The extractions were made with 1,000 ml. of benzene at 270°C. and 560 lb. sq. in. for 8 hours. After each extraction the residue was washed twice with 1,000 ml. of fresh benzene, and the residue from the filtration of the extract solution and washings was returned to the extractor before preheating again.

The results of this series of preheatings and extractions are given in Table 2.

TABLE 2.

Relation between Temperature of Preheatings and Formation of Soluble Product.

Preheating Temperature. ° C.	Weight of Product. Gm.	Per Cent. on Ash-free Basis.	
		Independent Result.	Additive Result.
Unheated	1.19	0.61	0.61
300.. .. .	5.46	2.79	3.40
320.. .. .	6.47	3.32	6.72
340.. .. .	22.62	11.57	18.29
360.. .. .	80.53	41.19	59.48
380.. .. .	40.97	20.60	80.08
400.. .. .	18.42	9.43	89.51
420.. .. .	1.60	0.82	90.33

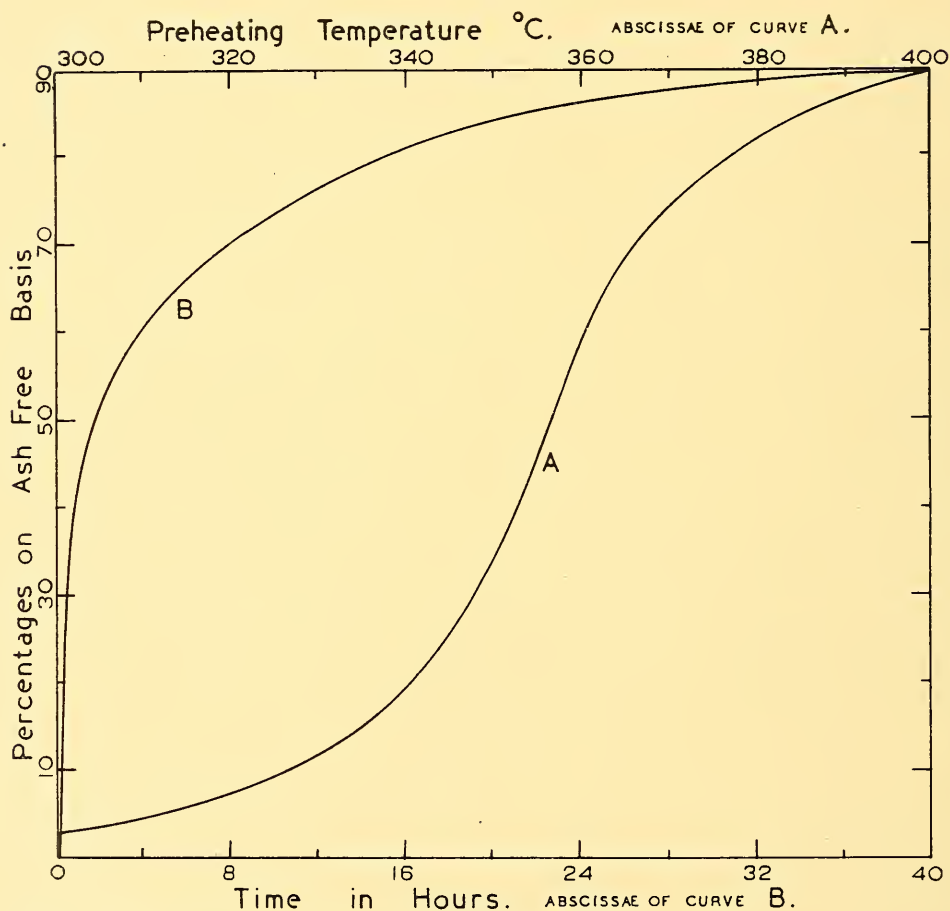


Fig. 2.—Diagram illustrating relations between temperature and formation of soluble product. Curve A, formation of soluble product with increasing temperature; Curve B, formation of soluble product at constant temperature of 360°C.

A very small yield of product is obtained by extracting the unheated torbanite, and comparatively small yields after heating at temperatures up to 340°C. There is a sudden increase in the formation of soluble products as the result of heating at 360°C., and the amounts fall off rapidly above 380°C. The quantity of product formed by heating at

temperatures above 400°C. is negligible, indicating that the conversion to the soluble form may be completed without exceeding a temperature of 400°C.

If these results are illustrated graphically (see Fig. 2, Curve A) the preheating temperatures and corresponding yields of soluble product being taken as abscissae and ordinates respectively, the curve obtained is very steep between 345° and 365°C., being concave upwards at the lower temperatures, and concave downwards at the higher temperatures. This curve between 300° and 400°C. is very similar in form to the curves between 400° and 500°C. for the evolution of volatile constituents during thermal decomposition, or retorting (see Dulhunty, 1941*b*). This means that the formation of the soluble, or intermediate product, and its subsequent thermal decomposition, both occur between narrow temperature limits separated by about 100°C. In retorting, it is recognized that the rate of heating must be gradual and carefully controlled between 400° and 500°C., while the oil vapours are coming off; but it is usual to increase the temperature rapidly up to 400°C., as no vapours are evolved below this temperature.

In view of the foregoing results, however, it would seem possible that the ultimate products of retorting may be influenced by the rate of heating between 300 and 400°C., while the organic matter is undergoing fundamental changes and the intermediate product is being formed.

A second experiment was carried out to determine the rate of formation of soluble material at constant preheating temperature, and the maximum amount which can be formed at a comparatively low preheating temperature. A portion weighing 250 gm. of the same torbanite as that used in the previous experiment was subjected to a series of preheatings at 360°C. under a pressure of 840 lb. sq. in. of benzene vapour for periods of $\frac{1}{4}$, $\frac{1}{2}$, 1, 4, 16 and 18 hours. The weight of soluble product was determined in the extract solution and washing obtained from each extraction.

The results of this experiment give the rate of formation of soluble material under the conditions of the product being removed as it is formed. This procedure was adopted in anticipation of later work involving extraction at the preheating temperature, in which case the product would be removed continuously. In examining the results, the amount of product extracted after each preheating, calculated on an ash-free basis, was plotted against the time of preheating, in the form of a graph as shown in Fig. 2, Curve B. The rate of formation of soluble product is very rapid in the early stages of heat treatment. About 50% of the total extractable material is formed during the first half hour, after which the rate falls off and becomes increasingly slow, the last 10% requiring about 24 hours. The total period of 40 hours, which was necessary for the formation of all the soluble product, would be greatly reduced by increasing the temperature of preheating, as the mean rate of formation appears to vary as a function of the temperature between 300° and 400°C.

Results recorded earlier in this paper indicate that a maximum of about 90% of the organic matter can be rendered soluble by preheating for comparatively short periods at temperatures up to 400°C. An important fact established by these experiments is that the same quantity of soluble product can be produced at 360°C. by prolonged heating. This would seem to imply a certain degree of homogeneity in the chemical nature of the organic matter of algal origin.

Acknowledgements.

In addition to acknowledgements made in the text of this paper, the author wishes to recognize the assistance of Mr. A. J. Tow in connection with the chemical treatment of extract solutions, and Mr. I. S. Haviland in routine testing.

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EXPLANATION OF PLATE VII.

Photomicrographs of torbanite powder and extraction residue. ($\times 30$.)

A and B.—Torbanite powders from Glen Davis and Baerami deposits, respectively, showing particles of translucent gelsite and retinosite.

C and D.—Residues from pressure-benzene extraction of Glen Davis and Baerami torbanites, respectively, showing minute grains of carbon and matrosite.